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Temperature, kinetic energy, and rotational temperature dependences for the reactions of $\text{Ar}^+ (^2\text{P}_{3/2})$ with O_2 and CO

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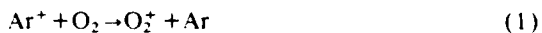
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Rate constants for the charge transfer reactions of $\text{Ar}^+ (^2\text{P}_{3/2})$ with O_2 and CO have been measured as a function of average center-of-mass kinetic energy $\langle \text{KE}_{\text{cm}} \rangle$ at three temperatures: 93, 300 and 543 K. The rate constants for both reactions were found to be slow at room temperature and to decrease with increasing kinetic energy or temperature in good agreement with previous data. No temperature dependence of the rate constants was found at any given $\langle \text{KE}_{\text{cm}} \rangle$ for both reactions, indicating that neither O_2 nor CO rotational excitation has much effect on the overall reactivity. The data also indicate that O_2 vibrational excitation does not increase the rate constant to the collisional value.

1. Introduction

The charge transfer reactions between Ar^+ ions and O_2 and CO ,



and



have been the subject of numerous studies, both experimentally and theoretically [1-14]. Although exothermic charge transfer between large molecular species are frequently fast, these simple systems involve only a small number of energy levels in the product molecular ions. The small density of states in these three atom systems in turn limits the number of curve crossings between the reactant and product potential curves resulting in small rate constants.

At room temperature the rate constants [15] are $k_1 = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_2 = 4.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The rate constants decrease with increasing kinetic energy [2,3] (below 0.3 and 0.9 eV for reaction (1)

and (2), respectively) and temperature [1,11]. At higher kinetic energies, the rate constants increase. This increase has been interpreted as a result of populating electronically excited $\text{O}_2^+ (a^4\Pi_u)$ and $\text{CO}^+ (A^2\Pi)$ [2,3] and has been subsequently proven for reaction (1) [3,11,13]. Cross sections for reactions (1) and (2) have been measured for the two spin-orbit states of Ar^+ [4,8,16].

Several groups have studied the energy distribution of the product ions of reactions (1) and (2). Marx and co-workers [5-7] found that at room temperature both products, O_2^+ and CO^+ , are produced vibrationally excited. Leone and co-workers [9,10] found the CO^+ product ion of reaction (2) to be highly vibrationally excited. The main channels are $v'' = 4-6$ and the rotational state distribution is characterized by a temperature on the order of 780 K. Scherbarth and Gerlich [12] found that at thermal energies the exothermicity of reaction (1) is used to populate a wide variety of ro-vibrational states of the electronic ground state of O_2^+ , the mean value of the internal energy being about 2 eV. With increasing collision energy ($> 0.55 \text{ eV}$) most of the reaction ex-

othermicity is released in the form of electronic excitation of the a⁴Π_u state of O₂⁺.

Early studies [2,3] attempted to explain the data by Franck-Condon factors or energy resonance. Later studies [8-10,12-14] show that at low collision energies reactions (1) and (2) proceed predominantly by an impulsive intimate collision mechanism rather than a single electron jump mechanism.

While a large amount of detailed work has been done on these reactions, there has been little if any discussion of the effect of the reagent rotations on the reactions. Recently, we have developed a technique that can assess the effect of rotations on reactivity. We have found that the charge transfer reaction of Ar⁺ with N₂ shows a strong dependence on the rotational temperature of N₂ [17,18]. The latter observance as well as the rather complicated mechanism of reactions (1) and (2) led us to undertake a study of the dependence of the rate constants of reactions (1) and (2) on the rotational temperature of O₂ and CO, respectively. In this paper we report the results and compare the energy and temperature dependences to previous experimental data.

2. Experimental

The measurements were made using the Phillips Laboratory (formerly the Geophysics Laboratory) variable temperature-selected ion flow drift tube apparatus (VT-SIFDT). The apparatus has been described in detail [19,20] and we will discuss here only those aspects that are relevant to the present study. Ar⁺ ions were generated in a relatively high pressure ion source and injected into a helium buffer. In a previous paper [17] it has been shown that Ar⁺ ions produced in this manner are in the ground state (²P_{3/2}). In this study no curvature was seen in any ion decay curve with varying reactant neutral gas flow rate lending support to that conclusion and indicate that we have essentially only ground state Ar⁺ in our experiment.

The rate constants were taken in the usual manner and will not be further described [19,20]. High purity O₂ (99.98%) and CO (99.997%) were used without further purification.

The average kinetic energy in the ion-neutral center of mass system, <KE_{cm}> in the drift tube is de-

rived from the Wannier expression [21] as

$$\langle \text{KE}_{\text{cm}} \rangle = \frac{(m_i + m_b)m_n}{2(m_i + m_n)} v_d^2 + \frac{3}{2} kT, \quad (3)$$

where m_i , m_b , m_n are the masses of the reactant ion, buffer gas and reactant neutral, respectively. v_d is the ion drift velocity and T is the temperature. The first term in expression (3) is the drift energy and the second term is the thermal energy. It has recently been shown in this laboratory that dependences of rate constants on the internal temperature of the reactant neutrals can be derived for a variety of monatomic ion-molecule reactions by measuring rate constants as a function of <KE_{cm}> at several temperatures [22,23]. The internal energy dependence is obtained by comparing rate constants at a given <KE_{cm}> but at different temperatures. Any difference outside of the relative error limit of ±15% can be attributed to the internal energy dependence of the reactant neutral.

3. Results and discussions

The rate constants of reactions (1) and (2) were measured as a function of <KE_{cm}> at three temperatures: 93, 300 and 543 K. The results are shown in figs. 1 and 2 for reactions (1) and (2), respectively. The relative uncertainties in the rate constants reported herein are estimated to be ±15% and absolute uncertainties are ±25% [19]. Data from a previous drift tube experiment at room temperature [2], from a variable temperature flowing afterglow [1], and from the CRESUS apparatus [11] at very low temperatures are shown for comparison. As can be seen in figs. 1 and 2 there is good agreement between our data and the previous results. The data show a negative dependence on energy as well as temperature.

The data taken at the three temperatures all lie virtually on the same line. Data taken at different temperatures but the same translational energy (interpolation is necessary) overlap and one cannot detect any differences outside of our experimental uncertainty. This indicates that the rate constants do not depend on the internal temperature of the neutral molecule [22,23]. Both neutrals have only one relatively high vibrational frequency. At 93 and 300 K,

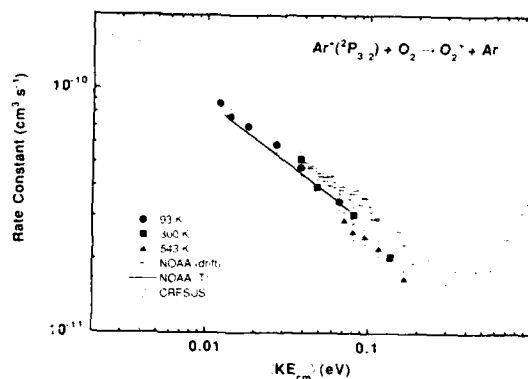


Fig. 1. Rate constants for the reaction of $\text{Ar}^+(^2P_{3/2})$ with O_2 as a function of $\langle KE_{cm} \rangle$. Closed circles, squares and triangles refer to rate constants measured in this study at temperatures of 93, 300 and 543 K, respectively. Previous data from a room temperature drift tube study [2] are shown as pluses, from a variable temperature flowing afterglow [1] as a solid line, and from a low temperature CRESUS experiment [11] as open circles. The error bars shown are the relative uncertainty and refer to the uncertainty in the ratio of two data points.

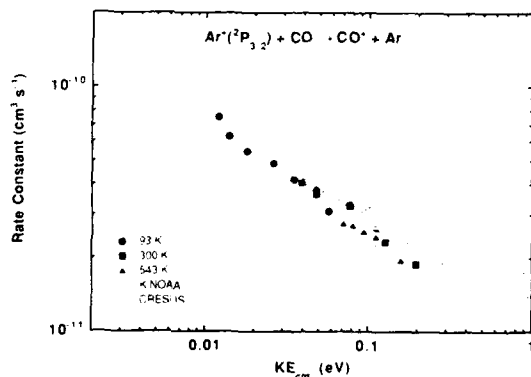


Fig. 2. Rate constants for the reaction of $\text{Ar}^+(^2P_{3/2})$ with CO as a function of $\langle KE_{cm} \rangle$. Closed circles, squares and triangles refer to rate constants measured in this study at temperatures of 93, 300 and 543 K, respectively. Previous data from a room temperature drift tube study [2] are shown as pluses and from a low temperature CRESUS experiment [11] as open circles. The error bars shown are the relative uncertainty and refer to the uncertainty in the ratio of two data points.

essentially all of the O_2 and CO molecules are in the ground vibrational state ($< 0.05\%$ of all molecules are excited). Therefore, the lack of a temperature dependence at the same translational energy between

93 and 300 K indicates that the rate constants are not strongly dependent on the rotational temperature of O_2 or CO.

At 543 K, 1.5% of the O_2 molecules and 0.4% of the CO molecules are vibrationally excited. The maximum effect these levels of excitation could have on the rate constant would be if the rate constants for vibrationally excited CO and O_2 proceeded at the collisional limit. If the $v=1$ rate constants were collisional, 10% and 30% increases (for CO and O_2 , respectively) would be found in the rate constants at a given kinetic energy for a temperature increase from 300 to 543 K. Therefore for CO, the lack of a temperature dependence at the same translational energy between 300 and 543 K only indicates that the rate constants are not strongly dependent on the rotational temperature of CO since the maximum effect that could be expected due to vibrational excited CO is within our error limits. No temperature dependence at the same translational energy was observed in the O_2 reaction between 300 and 543 K. This lack of dependence indicates that vibrational excitation does not increase the rate constant to a value within approximately a factor of two of collisional or we would have observed a change in the measured rate constant (assuming that the lack of a rotational energy dependence observed between 93 and 300 K also holds between 300 and 543 K). We conclude that the rate constants are not strongly affected by rotational energy and in the O_2 reaction a very large positive vibrational effect can be ruled out as well.

The lack of a rotational dependence in the present systems is in contrast to the charge transfer reaction of Ar^+ with N_2 where an appreciable rotational effect was found [17,18]. The rate constant for the reaction of Ar^+ with N_2 increases with increasing energy. The increase is due to the major product channel being slightly endothermic, i.e. $\text{N}_2^+(v=1)$. Rotational energy was found to be equally efficient at promoting the effectively endothermic charge transfer. This was determined from the fact that the rate constant was found to depend on the total energy of the reaction, i.e. the sum of translational and rotational energy.

In order to test if total energy controls these reactions we have replotted the rate constants as a function of total energy. Fig. 3 shows a plot of the

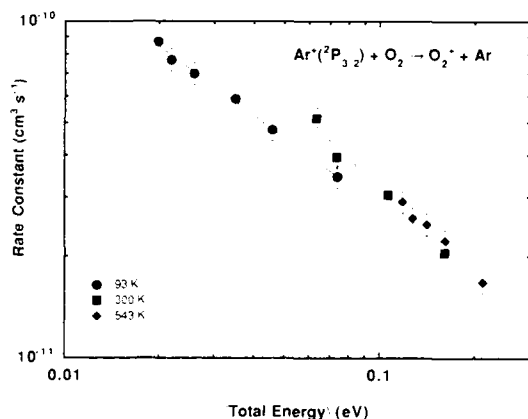


Fig. 3. Rate constants for the reaction of $\text{Ar}^+(^2\text{P}_{3/2})$ with O_2 as a function of average total energy. Closed circles, squares and triangles refer to rate constants measured in this study at temperatures of 93, 300 and 543 K, respectively. The error bars shown are the relative uncertainty and refer to the uncertainty in the ratio of two data points. Least-squares lines are drawn through the data.

rate constants for the reaction of $\text{Ar}^+(^2\text{P}_{3/2})$ with O_2 as a function of total energy. There may be a hint of a dependence on total energy in that the higher temperature rate constants are slightly larger than the lower temperature rate constants at a given total energy. However, the difference is within our error limits and therefore no definitive conclusion can be made. The lack of a temperature dependence of the rate constants at either a fixed $\langle \text{KE}_{\text{cm}} \rangle$ or total energy indicates that the method is not sufficiently sensitive to determine if the rate constants have no dependence on the rotational temperature or simply depend on total energy. The reaction of $\text{Ar}^+(^2\text{P}_{3/2})$ with CO behaves similarly.

The data taken by the CRESUS machine refer to neutrals at low rotational energy [11]. If our data are extrapolated to lower temperatures, it appears that the CRESUS data are slightly higher. This difference is, however, within the combined uncertainty of the data sets and again no conclusions on how rotational temperature influences the reactivity can be made from the comparison. Therefore, we conclude that rotational energy does not play a major role in determining the rate constants for reactions of Ar^+ ions with O_2 and CO, but a minor role cannot be excluded.

Our results and the wealth of experimental data quoted in the paper lead to the conclusion that both reactions (1) and (2) are very similar and proceed by the same mechanism and therefore will be discussed together.

The mechanism of reaction (1) has been discussed in detail by Kato [8] and that of reaction (2) by Lin et al. [10]. They conclude that the experimental results are better explained by a surface crossing at close approach, rather than by consideration of strict Franck-Condon factors or energy resonances.

Both reactions are characterized by energy being transferred from one form to another. At room temperature, Parent et al. [7] found that 51% and 68% of the exothermicity is converted into internal excitation of the product ions O_2^+ and CO^+ , respectively. Scherbarth and Gerlich [12] found that at thermal energies the exothermicity of reaction (1) is used to populate a wide variety of ro-vibrational states of the electronic ground state, the mean value of the internal energy being approximately 2 eV. Leone and co-workers [9,10] found that for reaction (2) the CO^+ product ion is vibrationally excited, with the main channels $v'' = 4-6$. The rotational state distribution could be characterized by a rotational temperature of approximately 780 K.

At elevated energies, transfer of translational to electronic excitation has been found for reaction (1) [1,3,12,13] and assumed also for reaction (2) [24]. For the back reaction, $\text{O}_2^+ + \text{Ar}$, electronic excitation of O_2^+ ions has been found to be very efficient in driving the endothermic direction [25,26].

In spite of this very efficient energy transfer we find no effect of the rotational energy on the rate constants of reactions (1) and (2). As explained above, this may be a consequence of a lack of sensitivity. While many aspects of these reactions have been studied as a function of many types of energy, at present there have been no studies that have examined the effect of the neutral vibrational energy except the crude results reported here for reaction (1). At present there are no convenient techniques for studying that dependence. However, an apparatus similar to that used in the present experiments but capable of reaching higher temperatures could address that question.

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